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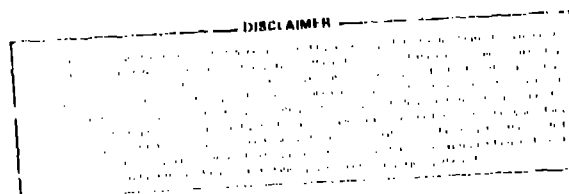
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TITLE: ELECTRON RESPONSE THEORY OF LATTICE VIBRATIONS: EMERGENCE OF CONCEPTS AND A GLANCE AT THE FUTURE

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**ELECTRON RESPONSE THEORY OF LATTICE VIBRATIONS:
EMERGENCE OF CONCEPTS AND A GLANCE AT THE FUTURE**

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I. INTRODUCTION

It is a rewarding experience to examine the long-term development of a particular field of natural science. From such a study one sees remarkable long-term correlations in the many and diverse individual efforts of researchers, correlations which are necessarily unobservable in the workings of the community at a fixed moment of time. There is a sense of progress which transcends the momentary chaos; there is a sense of achievement in the face of day to day frustration. It is also of interest to examine the motivations which have operated at various times along the path of development; here one sees how the specifically human attitude exerts an overall control on the shape of scientific accomplishment.

The problem we consider is lattice dynamics, or the theory of phonons. This is an extremely complicated problem, in which the motion of all the particles in the system, the nuclei and the electrons, are coupled. When faced with any problem of such complexity, it seems that physicists will invariably start by decoupling into single particles, and then study the effects of turning on various interactions, one at a time. Thus in the early 1900's, people were quite certain that the electrical and optical properties of metals resulted from

the presence of a few electrons which were nearly independent of the crystal, or were coupled only through a Boltzmann collision term, and were free to respond to applied fields. In 1918 the cohesive energy of the alkali halides was understood in terms of the attractive Madelung energy of a lattice of point ions,¹ and the compressibility was explained by a short-range repulsion which Born realized was due to the "inner structure of the ions."²

A whole new level of understanding was opened up by the work of Schrödinger in 1926. This "new quantum mechanics" was quickly applied to the problem of molecules and solids. Born and Oppenheimer wrote their famous paper in 1927;³ they were thinking specifically of molecules, but their derivation of the adiabatic approximation holds for a general system of nuclei and electrons. The adiabatic approximation means that, to a certain degree of approximation, there is no excitation of electrons from one state to others, but the total electronic state deforms progressively, as the nuclei move. Except for the simplest molecules, it is doubtful if anyone in those days seriously considered the possibility of actually solving the Schrödinger equation for the electronic state as a function of the nuclear positions, and of thus determining the potential which governs the motion of the nuclei. For solids, the result of the Born-Oppenheimer work was to provide a formal justification for separating the nuclear and electronic motion; this set the stage for the separate development of two almost-independent disciplines in solid state physics: lattice dynamics, and the electronic structure of crystals. We consider lattice dynamics in the following Section. In the electronic structure problem, the aim is to solve approximately the Schrödinger equation for the electrons in the fixed potential of a crystalline array of ions or nuclei. Slater started his long career in this discipline in the years immediately following Schrödinger's papers, and by 1930

we had the Hartree approximation, the determinantal wave function, and the Hartree-Fock equations.⁴

The fascination of solid state physics today is that we are finally able to put the pieces together: we are uniting the two disciplines which were formally separated in 1927. The process of development up to today is traced in the following discussion, and some implications for the future are presented.

II. LATTICE DYNAMICS

We turn to a brief sketch of the history of lattice dynamics in its primitive form. From the beginning, the motivation for studying the motion of the atoms in a solid was to understand the thermal energy associated with this motion. The empirical rule of Dulong and Petit for the heat capacity of solids was stated in the year 1819, as near as I have been able to determine. According to this rule, the heat capacity is $3R$ per mole, and I think people were pretty clever to figure this out so long ago. To understand this value of the heat capacity, we only need to count the number of degrees of freedom for translational motion of the atoms, and assign the classical equipartition energy to each degree of freedom. But later, the heat capacity of solids was observed to decrease toward zero at low temperatures, and this was explained as an effect of quantum statistics by Einstein in 1907.⁵ There was still a noticeable discrepancy between experiment and theory at the lowest temperatures, and this was explained by Debye in 1912.⁶ Debye's model takes the modes of vibration of a solid to be those of an elastic continuum, with a short-wavelength cutoff chosen to obtain the right number of degrees of freedom. The model is characterized by a particularly simple frequency distribution function, which allows statistical mechanical sums over normal modes to be transformed to very simple integrals

over frequency. In this way the Debye model gives a universal curve of heat capacity as a function of temperature, scaled for each material by its own characteristic temperature, and Debye showed in his original paper that his function gave an excellent account of the measured heat capacities for many solids. So well did Debye's elastic continuum model agree with experiment, that it had the effect of removing the motivation for further theoretical work for the next twenty years.

It is well known that there was also published at the same time a theory which took into account the atomic structure of real solids. This was the 1912 paper of Born and von Kármán,⁷ who solved the prototype lattice dynamics problem of a linear diatomic chain with nearest-neighbor harmonic forces. In the following year they also showed that their atomic model in three dimensions should give the same low-temperature T^3 behavior of the heat capacity as does the Debye model. But every theory is an approximation, and physicists have a strong tendency to use the simplest theory as long as it agrees with experiment. Meanwhile, however, experimentalists are always refining their measurements. By the early 1930's, measured heat capacities showed deviations from the Debye model; such deviations were customarily shown in graphs of the effective (experimental) Debye temperature as a function of temperature. The convincing explanation was given by Blackman,⁸ who showed by numerical calculations that atomic models could give variations in the effective Debye temperature, similar to the variations seen in experiments. It is of interest to note that Blackman was encouraged in his work by the ubiquitous Born. Finally in 1940-41 came Kellermann's calculations on NaCl.⁹ Kellermann took realistic forces between rigid ions, namely Coulomb interactions between point charges, plus nearest-neighbor central repulsion, and calculated the frequency distribution function and hence

the heat capacity. His result, Figure 1, shows the variation of Debye temperature due to phonon dispersion in the NaCl acoustic branches, and the calculation is in beautiful agreement with experiment. With this work, the discipline of lattice dynamics was securely established.

Of the many lattice dynamics calculations which followed, one is of particular interest because of its artistic ingenuity. Leighton¹⁰ wrote down the secular equation for a two-force-constant model for a face-centered-cubic lattice. He then proceeded to carve plaster-of-Paris models of the constant-frequency surfaces, and to determine the frequency distribution function by measuring the volume enclosed between successive surfaces. The volume measurement was accomplished by weighing the models in air, and also submerged in water. The computation gave a good account of the phonon dispersion effects on the Debye temperature of silver. When I think of this work, I picture a patient man sitting on a lab stool, white smudges of plaster dust on his knees and sleeves, carved models arranged around the work area, and he is leaning over the bench sculpting a curved surface with strokes of a scalpel - and he smiles as he works.

An event of great importance took place in 1955; that was the announcement by Brockhouse and Stewart of the first measurement of a phonon frequency and wavevector by inelastic neutron scattering.¹¹ Since that time, this technique has provided us with a great deal of highly accurate information, through the measurement of phonon spectra in a great variety of crystals. Since these data provide the most direct test of harmonic lattice dynamics theory, the emphasis of theory has shifted away from computing the heat capacity, and toward detailed studies of the complete set of phonon dispersion curves in high-symmetry directions. On the other hand, computation of thermodynamic functions is still quite

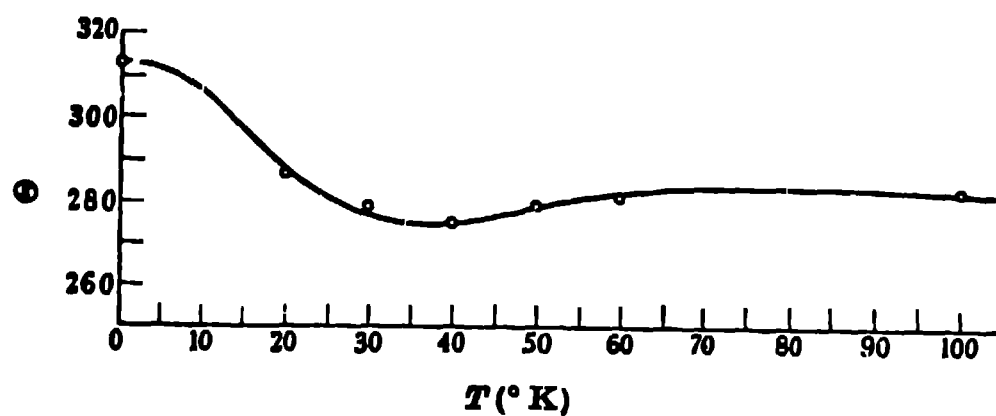


Figure 1. Temperature dependence of the Debye temperature for NaCl [from E.W. Kellermann, Proc. Roy. Soc. A178, 17 (1941)]. Smooth line is from experimental heat capacity, circles are Kellermann's calculation.

useful in testing theories which go beyond harmonic lattice dynamics, as for example in electron-phonon interaction effects. We note that the modern method of calculating thermodynamic functions does not use the frequency distribution function, but goes back to the original statistical mechanical expressions, and evaluates directly the Brillouin-zone sums of functions of the phonon frequencies and eigenvectors.¹²

In the study of ionic crystals, the idea of electron response in lattice dynamics was introduced by allowing the ions to deform as they move. In the time of Kellermann's work, it was known that the elastic constants of alkali halides satisfy reasonably well the Cauchy relations, which is consistent with rigid ions. But there was something wrong with the optical behavior of rigid ions, and people were already studying polarizable ion models; this led eventually to the development of shell models, which have been widely applied and are still in use today. In 1961 Tolpygo¹³ and Mashkevitch,¹⁴ using quite different philosophical approaches, arrived at quantum mechanical justifications of shell model equations. But it was in the study of metals where the theory of electron response was developed in its greatest simplicity, and with far reaching consequences; we turn next to that episode.

III. METALS AND THE DIELECTRIC FUNCTION

We begin the metals story with Wigner and Seitz in 1933.¹⁵ They undertook to solve the Schrödinger equation for the conduction electrons in metallic sodium. To approximate the problem they considered a single Na^+ ion at the center of an atomic polyhedron; for the Na^+ potential they used an empirical central potential fitted to atomic term values; they replaced the polyhedron by a sphere, neglected all potential from outside the sphere, and solved for the 3s

electron function with gradient zero on the sphere surface. This solution was supposed to represent the lowest-energy conduction state, and Wigner and Seitz then assumed the higher conduction states had free-electron energies relative to this lowest state. This remarkably simple picture of the electronic structure of the crystal gave a good account of the cohesive energy, the equilibrium lattice constant, and the compressibility of sodium. The magnitude of the numerical work is seen from the following interesting quote from the 1933 paper of Wigner and Seitz: "The calculation of a wave function took about two afternoons, and five wave functions were calculated on the whole."

A few years later, Fuchs¹⁶ showed that the same physical picture of the electronic structure can account for the cohesive energy and the elastic constants of Cu. An important contribution was made by Bardeen¹⁷ in his study of the electrical conductivity of monovalent metals. Bardeen noted that the perturbation potential acting on an electron, as a result of the motion of the ions, is the change in the potential of the ion system plus the change in the self-consistent field of the electrons. He further showed that this total potential is just the bare-ion potential screened, and he represented the screening with a dielectric function. After a long delay due to the war, progress resumed with the work of Toya in 1958.¹⁸ Toya formulated the lattice dynamics problem in terms of a diagonal dielectric function; he used Bardeen's screened-ion potential, with a free-electron evaluation of the dielectric function and approximate corrections for exchange and correlation, and calculated phonon dispersion curves for Na. The theory contained two parameters which were fitted to certain data for Na, and the computed phonon curves turned out to be in good agreement with inelastic neutron scattering measurements, published some years later. It is noteworthy that Toya also made calculations for Cu, with similar success.

It was a small step from the theory of Toya to pseudopotential perturbation theory. Nevertheless this step exerted a profound influence on the direction of metals theory, because of the remarkable simplicity of the pseudopotential formulation. In 1964, Harrison¹⁹ calculated the phonon frequencies of Al from orthogonalized-planewave form factors, and in 1965 Sham²⁰ produced an ultimately simple local-pseudopotential formulation from which he evaluated the phonon frequencies for Na. In the following years there appeared a major worldwide effort to apply this theory to all aspects of metal physics.

The physical basis of pseudopotential perturbation theory is as follows. The electrons in the metal are divided into two groups, the core electrons which move rigidly with the nuclei, and the conduction electrons which deform significantly as the nuclei move. The conduction electrons must be orthogonal to all the core electrons; when this requirement is introduced explicitly into the conduction-electron Schrödinger equation, the problem is transformed into a perturbation problem whose solutions are pseudo-wavefunctions and true electron energies. Because the pseudopotential can be treated as a perturbation, it is easy to study the total system energy for arbitrary positions of the nuclei. This allows the theory to be applied to problems beyond harmonic lattice dynamics, such as anharmonic effects and even liquids. The list of properties which can be reasonably accurately computed from pseudopotential theory is truly impressive; it includes the shape of the Fermi surface, the pressure dependence of the Fermi surface, the cohesive energy, the most-stable crystal structure, defect energies, the phonon spectrum and phonon Grüneisen parameters, the frequency-dependent optical properties, resistivity of liquid metals, structural phase change due to a change in temperature, electron-phonon enhancement of the

electronic heat capacity, electronic thermal expansion, and the superconducting transition temperature. The conclusion, which was clear by 1970, is that for those simple metals for which pseudopotential perturbation theory should apply, a fundamental unification of a wide range of solid state theories had been achieved. As an illustration of the kind of results produced in those days, I show in Figure 2 some calculated phonon dispersion curves for Al, solid lines, compared with measured values which are the dots.

The last major development up to the "present time" in the theory of lattice dynamics was the presentation by Sham²¹ in 1969, and by Pick, Cohen, and Martin²² in 1970, of the formal theory which is called the microscopic theory of lattice dynamics, or the dielectric function method. The two works were overall quite similar, and shared the following characteristics: they were designed to apply specifically to insulators, the electron-nuclear potential was taken as the Coulomb potential of point charges, the dynamical matrix was expressed explicitly in terms of the inverse dielectric function, and both papers derived in microscopic terms the acoustic sum rule and the Lyddane-Sachs-Teller relation. Some interpretive comments about the microscopic theory might be useful. First, the theory presented by Sham and by Pick, Cohen and Martin is valid, with only minor modification, for metals as well as insulators. Further, the bare nuclear potential can be replaced throughout by an ion core potential. There are three different but equivalent ways in which the physical content of the acoustic sum rule can be stated: it is the requirement that the acoustic phonon frequencies go to zero as the wavevector goes to zero; it is the requirement that the coupled system of nuclei (or ions) and electrons be translationally invariant; it is a condition on the long wavelength behavior of the non-local dielectric function, or any of the polarizability functions related to

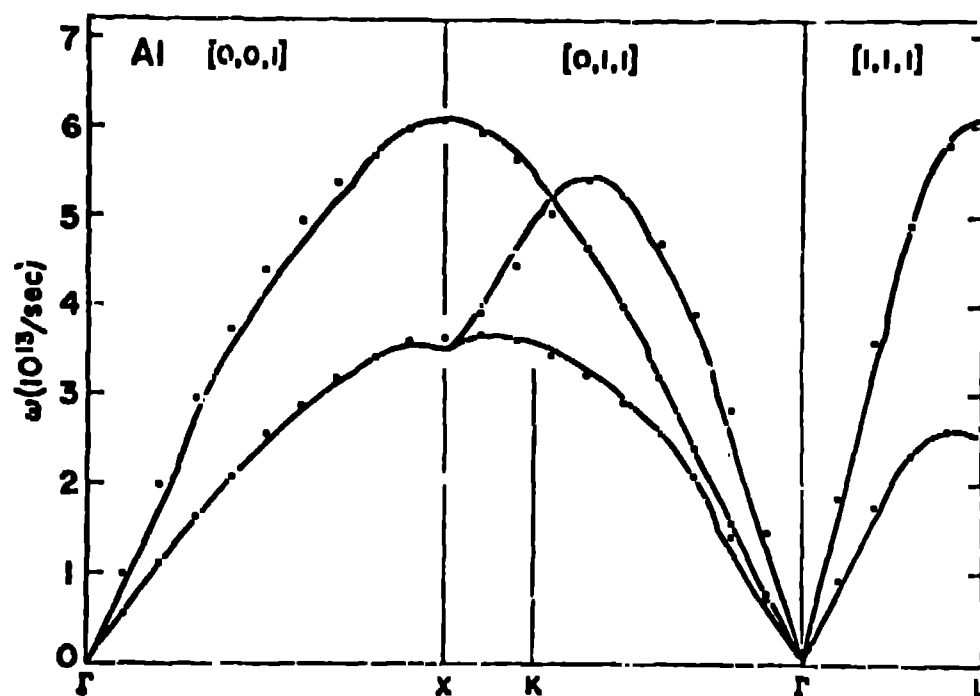


Figure 2. Phonon frequencies for Al [figure is from D.C. Wallace, Phys. Rev. 187, 991 (1969)]. The lines are calculated from pseudopotential theory, the dots are from experiment.

it. Finally, an essential difference between the electron response of metals and of insulators is easily pictured in terms of the dielectric-function formulation. If one considers a lattice of nuclei, or positive ions, in a rigid negative charge distribution, the longitudinal acoustic mode at zero wavevector has frequency equal to the plasma frequency of the nuclei. If now the negative charge is allowed to deform, that is to screen the motion of the nuclei, then the longitudinal acoustic mode frequency at zero wavevector is reduced to zero. For a metal this reduction can be accomplished with only diagonal screening, that is, when only diagonal elements of the dielectric function are considered. This is because in a metal the energy gap between occupied and unoccupied electronic levels is zero, which makes diagonal components of the dielectric function go to infinity in the long wavelength limit. On the other hand, for an insulator there is an energy gap in the electronic spectrum, the dielectric function remains finite, and the longitudinal acoustic mode frequency cannot be reduced to zero by diagonal screening alone. In other words, to satisfy the acoustic sum rule, a diagonal dielectric function is sufficient in metals, while in insulators the off-diagonal elements must be kept.

IV. THE PRESENT

This brings us to the present time. By the present, I mean the decade which has just closed, the decade of the 1970's. This period has been characterized by a widespread application of the microscopic theory of electron response to solid state problems. I will briefly describe the trends, the flavor of this activity; we shall have the good fortune to hear of the details from other speakers at this meeting.

An important aspect of the present period is the maturity of the theory of electronic structure of solids. After four decades of development under the leadership of John Slater, and the work of his students, and the work of their students, with APW and statistical exchange and the use of large computers, we now have detailed solutions in the one-electron approximation for practically any crystal of interest. By the early 1970's it was possible to calculate by this theory the cohesive energy, equilibrium lattice spacing, and compressibility of elemental crystals.²³ The availability of good electronic structures is proving now to be extremely valuable in developing the microscopic theory of electron response; this theory is, after all, an explicit statement of the fact that the electronic structure changes in response to an applied perturbation. This connection has encouraged a healthy increase in interdisciplinary study among solid state physicists today.

One problem of interest is in connection with superconductivity. There is a deep relation between the microscopic theory of phonons and the Bardeen-Cooper-Schrieffer theory of superconductivity. Both have at base the screened electron-ion interaction; in phonons this enters through the screened ion-ion interaction; in superconductivity it enters through the phonon-mediated electron-electron interaction. Now there is an experimental correlation between the appearance of anomalies in the phonon dispersion curves, and high superconducting transition temperature. The fact that this subtle problem is being studied on the level of the electron-ion interaction and the dielectric function shows the present level of sophistication of the theory.

There has been much work in the 1970's on covalent materials. A major theoretical device in this area is pseudopotentials, which may be determined to re-

produce accurate band-structure calculations, but which are not treated as a perturbation. Calculations have been done of the frequency-dependent optical properties, showing the importance of local-field corrections, which are the effect of off-diagonal elements in the dielectric function. The phonons, however, are much more difficult to calculate than the optical properties. This great difficulty was cause for several years of frustration in the theory of phonons, until finally there appeared some remarkable approximations which greatly simplify the computation, and which appear to give amazingly good results. These approximations are: the use of special point sums, say with 1 or 2 or 4 points, to represent Brillouin zone sums, and the replacement of perturbation-theory energy denominators in such a way that one sum over states can be carried out analytically, by completeness. One has the feeling that to learn why such methods should work will be to gain some new insight into the nature of electron response. An example of the kind of results obtainable is shown in Figure 3, a comparison of measured and calculated phonon frequencies for Si. The calculation, solid lines, is based on a moment expansion of the dielectric function.²⁴

As a final comment on the present situation, it may be noted that we have come to a slightly generalized view of the adiabatic approximation. What we do is to write the Hamiltonian for the system of electrons and nuclei, formally solve for the adiabatic motion, where the electrons remain at all times in their groundstate, and then treat the nonadiabatic terms as a perturbation. The perturbation can be expressed as a series in electron-phonon interactions, and given corrections in second order to the electron energies, and to the phonon energies.¹² In this way one calculates nonadiabatic corrections to the normal state in metals. Some observations about this theory which should be kept in mind: it is presumably asymptotic; the perturbation series is expected to

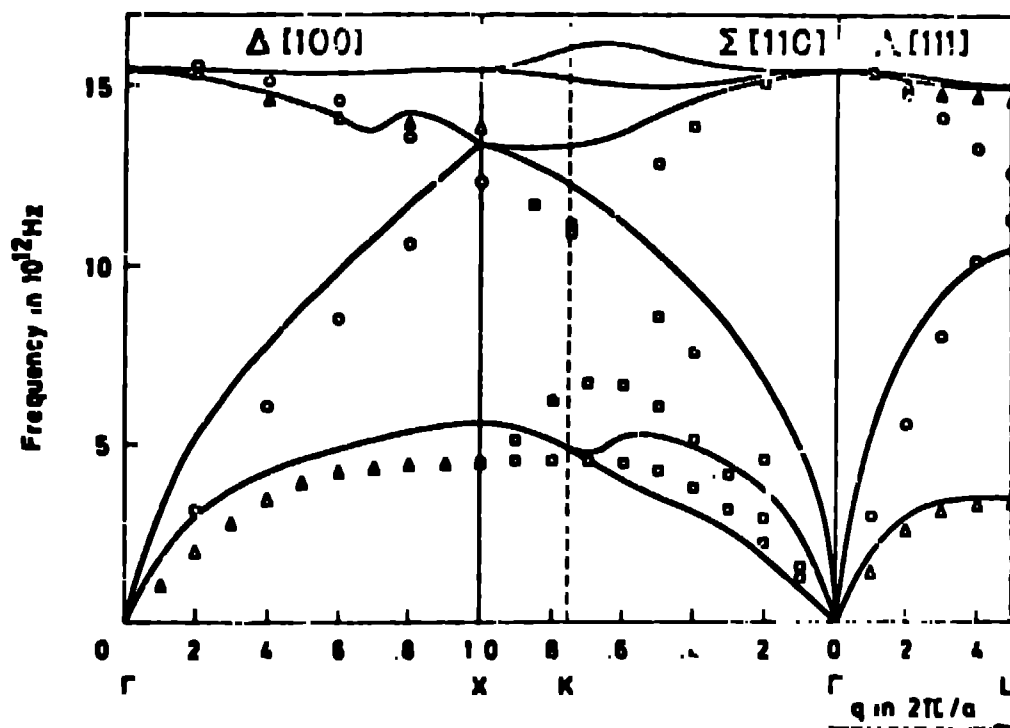


Figure 3. Phonon frequencies for Si. Solid lines are calculated, open symbols are from experiment [the figure is from P.E. Van Camp, V.E. Van Doren and J.T. Devreese, Phys. Rev. Lett. 42, 1224 (1979)].

diverge because of the presence of the superconducting groundstate;²⁵ the nonadiabatic Hamiltonian contains terms of all orders in the electron-phonon interaction. Hence an infinite order calculation of the first-order electron-phonon term, such as Migdal²⁶ has done, is not sufficient for a real metal in strong coupling. One hopes not to have to deal with strong coupling in practice; in this connection we note that, in practical computations, the electron-phonon interaction effects depend on the details of the adiabatic solution which has been obtained.

V. THE FUTURE

Since the new quantum mechanics was published in 1926, our understanding of the physics of dense systems of nuclei and electrons has steadily improved, at a respectable pace. And we can say today what was undoubtedly said most of the time along the way: It is an exciting time in solid state physics.

One area in which there will probably be increased effort in the future, and corresponding theoretical success, is in the study of liquids and amorphous materials, of their electronic structure, and properties such as transport coefficients, melting, and diffusion. And, spurred by controlled-fusion research and astrophysical applications, there should be advances in the theory of dense systems at extremely high pressures and temperatures. On another front, as the standard one-electron theory becomes incorporated into a wider range of problems, there will be opportunities for new progress in many-electron theory. In this connection there is a well-known theorem of Hohenberg and Kohn²⁷ which holds a fascination for many-body physicists. The theorem states that the energy of a system of electrons in the presence of an arbitrary fixed potential is a functional of the electronic density, and the part of the energy not

depending explicitly on the external potential is a universal functional, and the correct groundstate electronic density minimizes the energy functional. This theorem has been used in a form which still requires self-consistent solution of a set of single electron equations,²⁸ but the attraction of the theorem is on a deeper level: from it one knows that it must be possible to find the groundstate of the system by solving a single equation for a single function, namely the electronic density. The problem is, we don't know the functional, so we don't know the equation to solve. But, looking again to the future, one can be sure that physicists will not be satisfied until this question is answered.

I have one comment of encouragement and admonition for the younger people in research today. I have often heard expressed the dim prophecy that any day now, computers will take over the rest of the work that needs to be done. "We will only have to program the Schrödinger equation, and giant computers will solve every problem in solid state physics." This is nonsense. That computer does not exist today, nor will it ever exist, as far into the future as I can see. The physics of many-particle systems is extremely complex; progress will always depend on the ability of the scientist to separate out and understand new aspects of the problem. This is hard work, but for those who expect the computer to do it for them, progress will surely stop.

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FIGURE CAPTIONS

- Figure 1. Temperature dependence of the Debye temperature for NaCl [from E.W. Kellermann, Proc. Roy. Soc. A178, 17 (1941)]. Smooth line is from experimental heat capacity, circles are Kellermann's calculation.
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